SERVICES & FACILITIES ANNUAL REPORT - FY April 2013 to March 2014

SERVICE	FUNDING	AGREEMENT	ESTABLISHED as S&F	TERM 2yr extended by 5yrs
FENAC	BLOCK	PR120021	2009	

TYPE OF SERVICE PROVIDED:

The Facility for Environmental Nanoscience Analysis and Characterisation (FENAC) provides a unique service meeting the needs of the 'environmental nanoscience' community. Originally envisaged as a service supporting the (eco)toxicological community investigating the biological impact of manufactured nanomaterials*, FENAC also underpins the wider environmental community looking at manufactured nanoparticle chemistry and transport, along with incidental (combustion, industry etc) and natural (microbial, weathering etc.) nanomaterials and research work into potential applications of nanomaterials in, for example, environmental remediation or alternative energy. FENAC provides access and analysis for relevant samples, helping FENAC users through the whole process from experimental design to data analysis, in a fully collaborative manner. For doctoral and postdoctoral researchers carrying out measurement and data analysis, the discussions during training have provided a sound basis for future work. In some years, FENAC has also trained researchers more formally through 2 day summer schools, also leveraging NERC Knowledge Exchange programmes and University of Birmingham support.

Professor Eugenia Valsami-Jones and Professor Jamie Lead were directors of FENAC during 2013-2014 and Dr. Iseult Lynch was Deputy Facility Director, Dr. Christine Elgy was facility manager and Dr Gillian Kingston provided technical support (5% FTE) within FENAC. The facility offers a unique combination of experimental, analytical and metrological methodologies and the expertise to deploy such methods appropriately. There is competitive access to FENAC, with submissions due every 6 months.

*Nanomaterials, defined as having at least one dimension between 1 and 100 nm, are of three types: manufactured (deliberately produced), incidental (accidentally produced) and natural (produced by natural sources). FENAC offers a unique, proven ability to characterise and interpret the physico-chemical properties of nanoparticles from all sources, including complex environmental matrices (e.g. organisms), for properties including size, aggregation properties, surface behaviour, dissolution and morphology. Using a multi-method approach, FENAC incorporates a number of methods grouped as:

Microscopy (atomic force microscopy (AFM), confocal laser scanning microscopy (CLSM) and electron microscopy, including scanning, environmental scanning, scanning tunnelling and transmission electron microscopy (SEM, ESEM, STEM and TEM));

Spectroscopy (electron energy loss spectroscopy (EELS), x-ray energy dispersive spectroscopy (X-EDS), x-ray photoelectron spectroscopy (XPS), fluorescence correlation spectroscopy (FCS), and inductively-coupled plasma – mass spectrometry (ICP-MS));

Separation (including field–flow fractionation (FFF), ultrafiltration (UF), analytical ultracentrifugation, (AUC), disc ultracentrifugation and dialysis);

Other techniques (including dynamic light scattering (DLS), nanoparticle tracking analysis (NTA), differential centrifugal sedimentation (DCS), x-ray diffraction for crystal structure and surface area measurements by BET).

ANNUAL TARGETS AND PROGRESS TOWARDS THEM

FENAC has provided support for 14 projects during the 2013-2014 year. Of these, four are completed and ten on-going. Method development was carried out on nanoparticle synthesis and further development has taken place in dialysis for separating dissolved ions from nanoparticles, with trials of a new system planned for the coming year. Additional method development continues to be undertaken in other research projects led by the FENAC Directors, ensuring the continuation of FENAC's leading role internationally. FENAC has been widely marketed and availability disseminated at conferences, workshops and other venues. Demand continues to be healthy, with increased numbers of new applicants from different areas of research. Seven research papers were published in 2013, and six conference papers presented.

SCORES AT LAST REVIEW (each out of 5)		Date of Last Review:		
Need	Uniqueness	Quality of Service	Quality of Science & Training	Average
5	4.5	4.5	5	4.75

CAPACITY of HOST ENTITY FUNDED by S&F	Staff & Status	Next Review (March)	Contract Ends (31 March)
20%	Professor Eugenia Valsami-Jones and Professor Jamie Lead (3 hrs/wk combined); Dr. Christine Elgy (100% FTE); Dr Gillian Kingston (5% FTE)	2017	2017

FINANCIAL DETAILS: CURRENT FY						
Total Resource Allocation	Unit Cost £k			Capital Expend £k	Income £k	Full Cash Cost
£128.605k	£0.503k per day	£0.04k per hour electron microscopy	£0.06k per 10 icp-ms samples			£137.61k

FINANCIAL COMMITMENT (by year until end of current agreement) £k				
2013-14 £128.605k	2014-15 £128.605	2015-16 128.605	2016-2017 128.605	2017-2018

STEERING COMMITTEE	Independent Members	Meetings per annum	Other S&F Overseen
FENAC	8	2	0

APPLICATIONS: DISTRIBUTION OF GRADES (current FY — 2013/14)													
	10	**9**	**8**	**7**	**6**	**5**	**4**	**3**	**2**	**1**	**0**	**R***	**Pilot**
NERC Grant projects*				1									
Other academic			2				2					1	1
Students			2	1		2							2
TOTAL 14			4	2		2	2					1	3

PROJECTS COMPLETED (current FY – 2013/14)												
	10 (α5)	**9**	**8 (α4)**	**7**	**6 (α3)**	**5 (α2)**	**4**	**3 (α1)**	**2**	**1 (β)**	**0 (Reject)**	**Pilot**
NERC Grant projects*												
Other Academic				1								1
Students												2

Project Funding Type (current FY – 2013/14) (select one category for each project)										
Grand Total	**Infrastructure**					**PAYG**				
	Supplement to NERC Grant *	**PhD Students NERC**	**PhD Students Other**	**NERC Centre**	**Other**	**NERC Grant***	**PhD Students NERC**	**PhD Students Other**	**NERC Centre**	**Other**
14	2	1	6		5					

Project Funding Type (per annum average previous 3 financial years - 2010/2011, 2011/2012 & 2012/2013)										
Grand Total	**Infrastructure**					**PAYG**				
	Supplement to NERC Grant *	**PhD Students NERC**	**PhD Students Other**	**NERC Centre**	**Other**	**NERC Grant***	**PhD Student NERC**	**PhD Student Other**	**NERC Centre**	**Other**
9.33		2	4	0.33	3					

User type (current FY – 2013/14) (include each person named on application form)				
Academic	**NERC Centre**	**NERC Fellows**	**PhD Students**	**Commercial**
27		**2**	**8**	

User type (per annum average previous 3 financial years - 2010/2011, 2011/2012 & 2012/2013)				
Academic	**NERC Centre**	**NERC Fellows**	**PhD Students**	**Commercial**
18.33	**1**	**0.33**	**6.67**	

OUTPUT & PERFORMANCE MEASURES (current year)

Publications (by science area & type) (calendar year 2013)										
SBA	**ES**	**MS**	**AS**	**TFS**	**EO**	**Polar**	**Grand Total**	**Refereed**	**Non-Ref/ Conf Proc**	**PhD Theses**
	3	**2**		**8**			**13**	**7**	**6**	

Distribution of Projects (by science areas) (FY 2013/14)							
Grand Total	**SBA**	**ES**	**MS**	**AS**	**TFS**	**EO**	**Polar**
14	**0.33**	**2.33**	**4.83**		**6.5**		

OUTPUT & PERFORMANCE MEASURES (per annum average previous 3 years)

Publications (by science area & type) (Calendar years 2010, 2011 & 2012)										
SBA	**ES**	**MS**	**AS**	**TFS**	**EO**	**Polar**	**Grand Total**	**Refereed**	**Non-Ref/ Conf Proc**	**PhD Theses**
	0.67	367		8.33			**12.67**	6	6.67	

Distribution of Projects (by science areas) (FY 2010/2011, 2011/2012 & 2012/2013)							
Grand Total	**SBA**	**ES**	**MS**	**AS**	**TFS**	**EO**	**Polar**
9.33		0.67	4	**1**	3.67		

Distribution of Projects by NERC strategic priority (current FY 2013/14)							
Grand Total	**Climate System**	**Biodiversity**	**Earth System Science**	**Sustainable Use of Natural Resources**	**Natural Hazards**	**Environment, Pollution & Human Health**	**Technologies**
14	**0.20**		**1.70**	**0.33**	**1.03**	**9.53**	**1.20**

**Either Responsive Mode or Directed Programme grants*

NOTE: All metrics should be presented as whole or part of whole number NOT as a %

OVERVIEW & ACTIVITIES IN FINANCIAL YEAR (2013/14):

General Given the scale of the nanotechnology industry and the importance that the EU attaches to the environmental and human health hazards, FENAC's operation has been of great interest to the NERC research community and to a range of governmental and industrial bodies, globally. There is also considerable interest in FENAC from researchers investigating natural and incidental nanoparticles. FENAC pioneered the concept that it is essential to underpin nanotoxicology research with the highest quality characterisation under relevant exposure conditions. This concept has also been adopted at European level where an infrastructure facility, equivalent to FENAC, now exists. FENAC produces high quality publications, numbering 28 at 31/12/13 with 566 citations to date and, through the activities of its Directors, has raised the profile of UK nanoscience globally. FENAC is also developing links with the STFC neutron (ISIS) and synchrotron (Diamond Light Source) Facilities. FENAC continues the support and development of high impact science and selected highlights are shown below. Initial commercial interest in FENAC for characterisation of manufactured nanomaterials is expected to increase when European legislation for the safe development of nanotechnologies emerges.

Methods, Training and Staff Development

Research workers on seven separate projects, including four PhD students, have spent typically between one and three weeks at FENAC for training in the last year. Discussion of nanomaterials characterisation data, obtained both at FENAC and outside, has benefitted researchers, with advice provided for interpretation. Nanoparticle synthesis methods, and improved methods for particle dissolution studies, have been developed. A method has been developed for quantification of cerium 140 by ICP-MS for tracing nanoparticles with stable isotopes. FENAC has also acquired the capability for quantification of the number and size of nanoparticles in solution with the purchase of an ICP-MS which, can be operated in single particle mode, as well as increasing the analytical capacity. Additionally, an ICP-OES has been purchased by Birmingham University, extending the FENAC capability in trace element quantification, as the original facilities were heavily oversubscribed. An autotitrator for the DLS has been obtained with NERC support, with a three-titrant dispensing unit automating measurement of size and zeta potential as a function of pH, conductivity or additive concentration. A Gel Electrophoresis system with imager has also been purchased for characterisation of organic molecules adsorbed onto nanoparticle surfaces and has been used extensively for FENAC projects. New method development carried out in both Lead's and Valsami-Jones's groups has continued to inform FENAC practices, maintaining the facility as an internationally leading nanoscience centre. Training was run jointly with the EU FP7 QualityNano research infrastructure with FENAC hosting provided hands-on access to key equipment. Instrument manufacturer, NanoSight, also trained researchers in the use of their instrumentation.

Publications

Four of the FENAC publications from 2013 are listed, with impact factors shown [ ].

1. M. Baalousha and J. R. Lead (2013) Nanoparticle Dispersity in Toxicology. Nature Nanotechnology 8**,** 308-309 [31.17]
2. O. Osborne, B. Johnston, J. Moger, M.A. Baalousha, et al. (2013). Effects of particle size and coating on nanoscale Ag and TiO_2 exposure in zebrafish (*Danio rerio*) embryos. Nanotoxicology 7, 1315-1324 [7.844]
3. M.E. Pettitt and J.R Lead (2013).Minimum physicochemical characterization requirements for nanomaterial regulation. Environment International, 52, 41-50. [6.248]
4. D.J. Lapworth, B. Stolpe, P. J. Williams, D. C. Gooddy, J. R. Lead (2013). Characterization of suboxic groundwater colloids using a multi-method approach. Environmental Science & Technology, 47, 2554-2561. [5.257]

SCIENCE HIGHLIGHTS.

1) Following on from the work at FENAC to characterise Biogenic Amorphous Calcium Phosphate (BHAP), a promising remediation material with up to 15x higher sorption capacities than that of commercially produced hydroxyapatite for radionuclides, small angle neutron scattering (SANS) was carried out at ISIS to examine size, shape, internal structure and spatial arrangement of BHAP growth over time. Preliminary data of BHAP saturated bacteria showed fractal cluster models (e.g. primary radii <10 Å, fractal dimensions around 2.7-2.8 and final cluster sizes between 150-350 Å).

Handley-Sidhu who was trained at FENAC to characterise BHAP, was invited to help run a 4 day intensive Environmental Radioactivity training course attended by MSc students from the Universities of Hokkaido, Tokai and Fukushima. Students carried out field sampling and monitoring at Iitate Village and analysed collected samples (soils, sediments, plants material) at the newly established Institute of Environmental Radioactivity, Fukushima University.

Figure 1. Handley-Sidhu at Fukushima University providing remediation training in Environmental Radioactivity

To take this further, a NERC Technology Proof of Concept award was granted in early 2014 for 'Biogenic metal phosphates: Low cost, high capacity and stable 'lockups' for the removal of radionuclides from groundwater and decontamination solutions (BioLock)' The aims are (1) To show technical feasibility by producing scalable, cheap BHAP materials for decontamination. (2) To validate BHAP as reactive barrier material for treating environmental levels of radionuclides in groundwater (in partnership with UK National Nuclear Laboratory). (3) To decontaminate Fukushima soils and remediation of soil washing (in partnership with the Japanese Atomic Energy Agency). (4) To show potential for permanent 'lockup' by determining site of incorporation and using leaching tests. *There is significant environmental and echonomic potential of this work both within the UK and internationally.*

2) Project work carried out by the British Geological Survey and FENAC has direct relevance for environmental toxicologists and scientists in developing an understanding of the fate of silver nanoparticles in suboxic environmental conditions, such as those commonly found in effluents from waste water treatment, and at the base of rivers. Silver is known to be harmful to organisms in the environment, but there is increasing use of silver nanoparticles for their antimicrobial properties in clothing and cleaning sprays. The nanoparticles can enter the wider environment through the water treatment system. Because the reaction of sulphide ions with silver nanoparticles has previously been shown to modify surface charge and dissolution rate, there is a common assumption that the nanoparticles with a sulphide surface coating are very stable and therefore low in toxicity, however, the experimental data to support

Figure 2. Typical TEM and AFM images of a) citrate capped silver nanoparticles in anoxic water containing $CaCl_2$, and additions of b) sulfide, c) humics, d) humics and sulfide

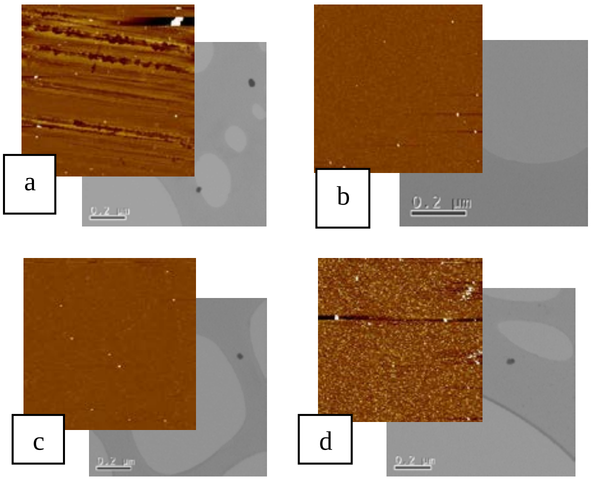
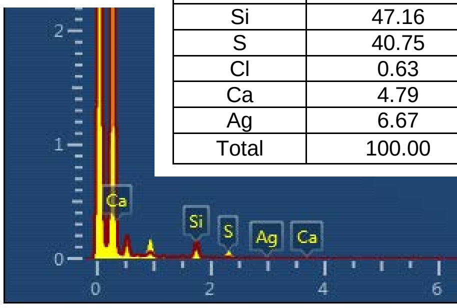


Figure 3. EDX data for citrate capped nanoparticles with sulfide ions, in water containing low levels of dissolved $CaCl_2$ under suboxic conditions: high concentrations of sulfide indicate an association with Ag.

Element	Silver Nanoparticle Atomic %	Background Atomic %
Si	47.16	91.89
S	40.75	4.70
Cl	0.63	0.84
Ca	4.79	2.57
Ag	6.67	0.00
Total	100.00	100.00



this assumption are limited. In this work the influence of naturally occurring humic substances in the interactions between nanoparticles and ions in natural waters is being examined for these systems. Silver nanoparticles were prepared at FENAC for use in this work using citrate and 10k PVP as capping agents for the two types of nanoparticles. Suspensions of the nanoparticles were prepared in synthetic suboxic water containing low levels of calcium chloride. Changes in size, shape and aggregation of silver nanoparticles in the presence of humic acid and/or sulphide ions were investigated to establish the influence of the medium on nanoparticle behaviour.

3) A project in collaboration with the University of Exeter has looked at the toxicity of cerium oxide nanoparticles (CeO_2 NPs). Because cerium can readily change oxidation states between Ce(III) and Ce(IV), CeO_2 NPs are widely used in catalysis and fuel cells and they are also used on an industrial scale as an additive in diesel fuel, and for polishing glass and silicon wafers. Following release to the environment, most NPs including CeO_2 NPs are predicted to pass to the water system. Toxicology studies have shown these nanoparticles can in some cases cause oxidative stress and in other studies have a protective effect against oxidation. This project has studied the effect of ingestion of CeO_2 NPs on a marine organism, *Corophium volutator* (the mudshrimp) that feeds on particulate matter from the sediment surface and from suspended particles, to assess the toxicity in an organism likely to be exposed to particulate material through feeding.
At FENAC, the CeO_2 NPs were characterised in pure water and in artificial seawater (ASW), the organisms' habitat in this study, to assess particle stability and any potential redox transformations.

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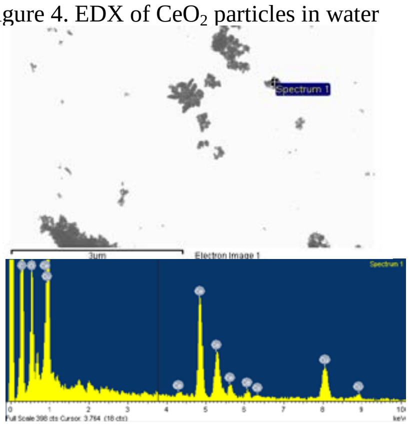
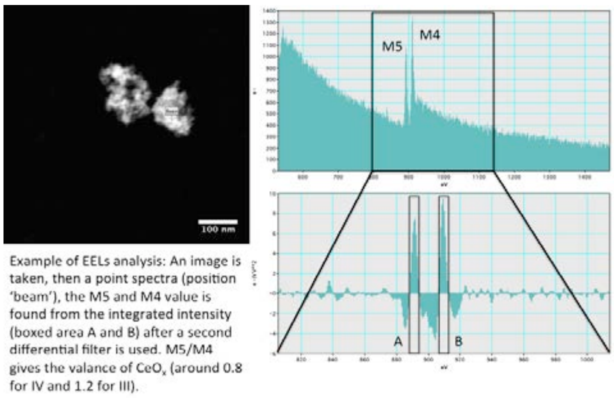
Figure 4. EDX of CeO_2 particles in water



Electron Dispersive X-ray (EDX) spectra (Joel 7000, Oxford EDX system). Show a clear cerium peak confirming the presence of CeO_2 nanoparticles (12.5ppm CeO_2 in Milli-Q water), and the associated spectra. The Cu peaks are from the sample support.

Figure 5. EELS analysis of CeO_2 particles in water



In the centre of particles the M5/M4 ratio indicates that particles in water are Ce(IV) (probably CeO_2) and in synthetic seawater are Ce (III) (probably Ce_2O_3). Line scans from the centre to the outside of particles on the edge of aggregates in ASW, but showed mixed valence: Ce(IV) and Ce(III)

The levels of ceria used were sub-lethal to *Corophium volutator* but some toxicity was observed. Redox cycling of the cerium oxide was demonstrated in seawater. A publication has been submitted from this work.

FUTURE DEVELOPMENTS: FENAC will continue to support research within the environmental ' nano' community and other relevant areas with environmental impact. Access to essential training through FENAC will continue through one-to-one laboratory support and in workshops, either on site or at relevant conferences and meetings, which will act as valuable outreach mechanisms.
In the coming year, method development for measurement of zeta potential under conditions of high salinity will be a priority with a review of the various techniques available. Further method development of dialysis for solubility measurements will also occur. Trials will also be conducted of surface area measurements for solids in suspension to assess their suitability for use within FENAC.
A new clean facility will be built to locate the single particle ICP-MS capability, and the three ICP instruments will be centralised within the FENAC main laboratory to improve efficiency.